

An analytic treatment of the first-order correction to the Poisson–Boltzmann interaction free energy in the case of counterion-only Coulomb fluid

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Abstract. We have computed the first-order (correlation) correction to the Poisson–Boltzmann result for the interaction energy of two charged surfaces immersed into a counterion-only Coulomb fluid. The cases of small and large coupling were amenable to analytic treatment in the saddle-point approximation.

1. Introduction

Electrostatic interactions between charged macroscopic surfaces immersed in an electrolyte are of primary importance in subjects as diverse as colloid stability or (bio)macromolecular assembly. They are usually evaluated in the mean-field (Poisson–Boltzmann) approximation that leads to repulsive forces if the two interacting surfaces are equally charged [1]. Recently much effort has been directed towards a consistent generalisation of the mean-field theory that would take into account also the thermodynamic fluctuations in the local charge distributions [2]. The importance of the correlation corrections to the interaction free energy can be assessed from the fact that in some physically realistic cases they can even reverse the sign of the interaction [3].

Though the most successful approaches to the correlation problem lead to theories of high numerical complexity [2] we have been able to devise an alternative, simpler, approach that in certain cases leads even to analytical results, while at the same time remains as close as possible to the original Poisson–Boltzmann treatment [4]. Our approach relies heavily on the use of the functional integral representation (the sine-Gordon transform) of the grand canonical partition function of the interacting Coulomb fluid and uses the standard methods of field theory [5]. It yields a quadratic fluctuation (correlation) correction to the mean-field results.

In this paper we shall show how the application of the saddle-point approximation to the grand canonical partition function of the counterion-only system bounded by two charged surfaces leads to analytically tractable results in the limiting cases of small and large couplings. The quadratic fluctuation corrections to the mean-field results will be evaluated with the help of the ζ -function technique [5]. The small-coupling limit will be reduced to an evaluation of a free particle propagator in a slab with additional boundary conditions on the borders, while the large-coupling limit will be reduced to a form basically equivalent to the symmetrised Pöschl–Teller propagator. Both propagators will be solved analytically, giving exact limiting forms for the interaction free energy.

2. Functional integral representation of the grand canonical partition function

We shall consider a dielectric of constant relative permittivity ϵ spanning the region $-\infty < z < \infty$. The slab $|z| \leq a$ is filled by mobile counterions of unit charge and absolute activity z_c . In order to ensure the stability of the system we assume that the walls at $z = \pm a$ are uniformly negatively charged with surface charge density σ . The magnitude of the surface charge is such that it ensures the overall electrical neutrality of the system. The configurational part of the Hamiltonian for this system can be written in the form

$$U_N = \frac{1}{2} \sum_{i \neq j} e_i e_j u(\mathbf{r}_i, \mathbf{r}_j) + \sum_i e_i \varphi_0(\mathbf{r}_i) \quad (2.1)$$

where $u(\mathbf{r}, \mathbf{r}')$ is the bare Coulomb interaction between two unit charges obtained as a solution of the Poisson equation

$$\nabla^2 u(\mathbf{r}, \mathbf{r}') = -\delta(\mathbf{r} - \mathbf{r}') / \epsilon \epsilon_0 \quad (2.2)$$

and $\varphi_0(\mathbf{r})$ is the external potential due to the fixed charges present in the system. The grand canonical partition function can now be expressed as

$$\Xi = \sum_{N=0}^{\infty} \left(\frac{z_c}{N!} \right)^N \int_{(V)} \exp(-\beta U_N) d^3 N \mathbf{r} \quad (2.3)$$

where β is the inverse thermal energy ($\beta = (kT)^{-1}$) and V is the volume of the region occupied by the counterions. We now proceed by applying the Hubbard-Stratonovich transformation to the expression (2.3), namely

$$\exp\left(-\beta \frac{1}{2} \sum_{i,j} e_i e_j u(\mathbf{r}_i, \mathbf{r}_j)\right) = \left\langle \exp\left(i\beta \sum_i e_i \varphi(\mathbf{r}_i)\right) \right\rangle_{\varphi} \quad (2.4)$$

where i is the imaginary unit. The average over auxiliary fields is defined as

$$\langle \dots \rangle_{\varphi} = \Delta(\beta) \int_{(N)} (\dots) \exp\left(-\frac{1}{2}\beta \sum_{i,j} \varphi(\mathbf{r}_i) u^{-1}(\mathbf{r}_i, \mathbf{r}_j) \varphi(\mathbf{r}_j)\right) d\varphi(\mathbf{r}_1) \dots d\varphi(\mathbf{r}_N) \quad (2.5)$$

with

$$\Delta(\beta) = (2\pi)^{N/2} (\det \beta u^{-1}(\mathbf{r}, \mathbf{r}'))^{1/2}. \quad (2.6)$$

This trick allows us to sum the expression (2.3) exactly, leading to the desired functional integral representation of the grand canonical partition function in the form [6]

$$\Xi = (\det \beta u(\mathbf{r}, \mathbf{r}'))^{-1/2} \int_{\{\varphi(\mathbf{r})\}} \exp(S(\varphi(\mathbf{r}))) \mathcal{D}\varphi(\mathbf{r}) \quad (2.7)$$

where $\mathcal{D}\varphi(\mathbf{r}) = \lim_{N \rightarrow \infty} d\varphi(\mathbf{r}_1) d\varphi(\mathbf{r}_2) \dots d\varphi(\mathbf{r}_N)$ and the action S is obtained as

$$S = -\frac{1}{2}\beta \epsilon \epsilon_0 \int (\nabla \varphi(\mathbf{r}))^2 d^3 \mathbf{r} + z_c \int \exp(-i\beta e_0 \varphi(\mathbf{r})) d^3 \mathbf{r} - \beta i \oint \sigma \varphi(s) d^2 s \quad (2.8)$$

where s is the radius vector along each surface at $z = \pm a$. In the above equation we have redefined the auxiliary field as $\varphi(\mathbf{r}) \Rightarrow \varphi(\mathbf{r}) + i\varphi_0(\mathbf{r})$ and renormalised the value of the absolute activity, namely

$$z_c \Rightarrow z_c \exp(\frac{1}{2}\beta N e_0^2 u(\mathbf{r}, \mathbf{r})) \quad (2.9)$$

where N is the total number of the counterions in the system and $u(\mathbf{r}, \mathbf{r})$ is the self-energy of each ion. Equations (2.7) and (2.8) define a field theory that we could, exploiting an obvious analogy, name the exp-Gordon theory. The action (2.8) is clearly nothing but the Poisson-Boltzmann free energy [7] evaluated at an imaginary value of the charges, $S = F_{PB}(ie_0)$, therefore the auxiliary fields $\varphi(\mathbf{r})$ could be interpreted as the local electrostatic potentials [6].

The 'classical equation of motion' corresponding to the exp-Gordon theory is clearly the Poisson-Boltzmann equation with an appropriate boundary condition that expresses the overall electrical neutrality of the system. Instead of just writing down the Poisson-Boltzmann equation we shall first of all introduce

$$u(\mathbf{r}) = \frac{\beta e_0^2 z_c}{\epsilon \epsilon_0} \exp(-\frac{1}{2} \beta e_0 \varphi(\mathbf{r})) \quad (2.10)$$

that will allow us to write the Poisson-Boltzmann equation in the plane-parallel geometry, where the mean potential depends only on the transversal coordinate (z), as

$$\frac{d^2 u}{dz^2} = -u_0^2 u + u^3 \quad (2.11)$$

where u_0 is the value of u at the midpoint between the two boundary surfaces, i.e. $u_0 = u(z=0)$. The electroneutrality condition (boundary condition) written in the new variables is

$$\frac{\partial u}{\partial \mathbf{n}} = \Gamma u(z = \pm a) \quad (2.12)$$

with

$$\Gamma = \beta e_0 \sigma / \epsilon \epsilon_0$$

where \mathbf{n} is the local surface normal[†]. Equation (2.11) is clearly nothing but the equation of motion of the φ^4 model; we have been, however, unsuccessful in establishing any sort of general transformation, valid also beyond the 'classical' regime (the mean-field regime in the statistical mechanical sense), between the counterion-only system (the exp-Gordon theory) and the φ^4 model.

As can be easily verified, the solution of (2.11) and (2.12) in the plane-parallel geometry, where z is the transversal coordinate, can be written in the form

$$u^2(z) = 2\alpha^2 / \cos^2(\alpha z) \quad (2.13)$$

where α is obtained as a solution of

$$\alpha \tan(\alpha a) = \Gamma. \quad (2.14)$$

This solution depends on the value of the dimensionless coupling constant (Γa) and we shall address two different limiting cases corresponding to small and large values of (Γa). The two limiting solutions of (2.14) are obtained as

$$\alpha a (\Gamma a \Rightarrow 0) \simeq \sqrt{\Gamma a} \quad (2.15a)$$

$$\alpha a (\Gamma a \Rightarrow \infty) \simeq \pi/2. \quad (2.15b)$$

[†] It should be noted at this point that Γ^{-1} and a are the sole intrinsic length scales of the counterion-only system and therefore the product Γa is the only dimensionless coupling constant that can be constructed.

The appropriate potential profiles are obtained by inserting these solutions into (2.13) and taking the indicated limits.

Finally let us just add that the interaction free energy corresponding to the mean-field solution can be derived straightforwardly in the form

$$\frac{F}{S} = 2\epsilon\epsilon_0 \left(\frac{kT}{e_0}\right)^2 [\alpha^2 2a + 2\Gamma \ln(1 + (\alpha/\Gamma)^2)] \quad (2.16)$$

where S is the area per surface. As will be shown in the next section the saddle-point approximation allows us to treat the mean-field and the fluctuation contributions to the free energy as additive.

3. The saddle-point method and the ζ -function evaluation of the functional determinant

Since the action of the exp-Gordon theory is not Gaussian no exact evaluation of the grand canonical partition function (Ξ) is possible and we are forced to use approximative methods to obtain fair estimates of the thermodynamic properties of the system. The quadratic fluctuation correction to the mean-field solution is obtained if we develop the action S , (equation (2.8)), up to second order in fluctuations around the solution $u = u(z)$. In this particular case the functional integral (2.7) is reduced to Gaussian integrations and can be evaluated exactly. This is the essence of the saddle-point approximation that consists of the following statement:

$$S = S_0 + \frac{1}{2} \iint \left(\frac{\delta^2 S}{\delta\varphi(\mathbf{r})\delta\varphi(\mathbf{r}')} \right)_0 \delta\varphi(\mathbf{r})\delta\varphi(\mathbf{r}') d^3\mathbf{r} d^3\mathbf{r}' \quad (3.1)$$

valid if the fluctuations in the local electrostatic potentials are small overall. The 'classical' (Poisson-Boltzmann) value of the action S_0 is obtained as $S(\varphi_0)$ where φ_0 is the solution of the PB equation that we have written in the form of (2.10). The thermodynamic potential, Ω , can now be obtained in an explicit form by executing the Gaussian integrations implied by (3.1):

$$\Omega = -kT \ln \Xi = -kTS_0 + \frac{kT}{2} \ln \det \left(\int u(\mathbf{r}, \mathbf{r}') \left(\frac{\delta^2 S}{\delta\varphi(\mathbf{r}')\delta\varphi(\mathbf{r}'')} \right)_0 d^3\mathbf{r}'' \right). \quad (3.2)$$

Clearly Ω is a functional of the generalised response operator

$$\left(\frac{\delta^2 S}{\delta\varphi(\mathbf{r})\delta\varphi(\mathbf{r}')} \right)_0 = u^{-1}(\mathbf{r}, \mathbf{r}') + \epsilon\epsilon_0 u^2(z) \delta(\mathbf{r} - \mathbf{r}') \quad (3.3)$$

with $u(z)$ being the solution of the 'equation of motion' (2.11). We have already shown that the functional determinant in (3.2) can be evaluated by the resolvent operator method in conjunction with a complicated coupling constant integral [4]. For our present purposes it is, however, much more convenient to use the sc zeta-function method [5] that will permit us to obtain analytical results in both large- and small-coupling limits.

The zeta-function method consists of the following [5]. If we construct a 'heat' function $G(\mathbf{r}, \mathbf{r}'; t)$ associated with an operator A by way of a differential equation ('heat equation')

$$AG(\mathbf{r}, \mathbf{r}'; t) = -\frac{\partial}{\partial t} G(\mathbf{r}, \mathbf{r}'; t) \quad (3.4)$$

satisfying the boundary condition $\lim_{t \rightarrow 0} G(\mathbf{r}, \mathbf{r}'; t) = \delta(\mathbf{r} - \mathbf{r}')$, and then define the ζ_A -function adjoined to the operator A by the integral

$$\zeta_A(s) = \frac{1}{\Gamma(s)} \int_0^\infty dt t^{s-1} \text{Tr } G(\mathbf{r}, \mathbf{r}'; t) \quad (3.5)$$

it is then straightforward to show that the determinant of the operator A can be expressed with the help of the $\zeta_A(s)$ as

$$\ln \det(A) = - \left. \frac{d\zeta_A(s)}{ds} \right|_{s=0}. \quad (3.6)$$

Returning now to our problem of evaluating the functional determinant of the generalised response operator (3.3) we are led to the following 'heat' equation

$$\int \left(\frac{\delta^2 S}{\delta \varphi(\mathbf{r}) \delta \varphi(\mathbf{r}')} \right)_0 G(\mathbf{r}, \mathbf{r}'; t) d^3 \mathbf{r}' = - \frac{\partial}{\partial t} G(\mathbf{r}, \mathbf{r}; t) \quad (3.7)$$

which after taking cognisance of the fact that $u(\mathbf{r}, \mathbf{r}')$ satisfies the Poisson equation, (2.2) leads to

$$\nabla^2 G(\mathbf{r}, \mathbf{r}'; t) - u^2(z) G(\mathbf{r}, \mathbf{r}'; t) = \frac{\partial G(\mathbf{r}, \mathbf{r}'; t)}{\partial t}. \quad (3.8)$$

The above equation would describe a quantum mechanical 'particle' moving in an external potential $u^2(z)$ in imaginary time. Taking now into account the definition of the ζ -function (3.5) we can derive the fluctuation part of the free energy (3.2) in the form [8]

$$F = - \frac{kT}{2} \frac{d\zeta_A(s=0)}{ds} = \frac{kT}{2} \int_0^\infty \frac{dt}{t} \text{Tr } G(\mathbf{r}, \mathbf{r}'; t) \quad (3.9)$$

where Tr is the trace operator. It will prove profitable to derive an alternative form of the free energy valid in the case that u is a constant, $u^2 = \lambda$. This case will be relevant while considering the small-coupling limit. We proceed as follows. First of all we note the identity derivable from (3.8)

$$\int_0^\lambda G(\mathbf{r}, \mathbf{r}'; t) d\lambda = -G(\mathbf{r}, \mathbf{r}'; t)/t.$$

Taking this into account we can rewrite (3.9) into the following form:

$$F = - \frac{kT}{2} \int_0^\lambda d\lambda \int_0^\infty dt \text{Tr } G(\mathbf{r}, \mathbf{r}'; t). \quad (3.10)$$

This result can be cast into an even simpler form that we shall need afterwards. Now since our system is translationally invariant in the (x, y) plane, we can introduce the Fourier transform

$$G(\mathbf{r}, \mathbf{r}'; t) = \int g(z, z'; Q, t) e^{iQ(s-s')} d^2 Q / (2\pi)^2. \quad (3.11)$$

Furthermore the function $g(z, z'; Q, t)$ can be expressed through its Laplace transform as

$$g(z, z'; Q, t) = \frac{1}{2\pi i} \oint_c e^{pt} g(z, z'; Q, p) dp$$

where c is the standard inverse Laplace transform contour. Inserting (3.11) into the energy formula (3.10) while taking into account the above definition we are finally led to the following form of the free energy:

$$F = \frac{kTS}{4\pi} \int_0^\lambda d\lambda \int_0^\infty Q dQ \operatorname{Tr} g(z, z'; Q, p=0) \quad (3.12)$$

where S is the surface area of the two interacting surfaces. This formula is most advantageous for systems that show plane-parallel symmetry.

4. The small-coupling limit ($\Gamma a \Rightarrow 0$)

In order to solve (3.8) in the small-coupling limit it will prove profitable to introduce the inverse Laplace transform (\mathcal{L}^{-1}) of the function $g(z, z'; Q, t)$ as

$$g(z, z'; Q, t) = \mathcal{L}^{-1}[g_p(z, z'; Q)].$$

With this ansatz the 'heat' equation in this limiting case can be cast into the form

$$\frac{\partial^2}{\partial z^2} g_p(z, z'; Q) - (Q^2 + 2\alpha^2 + p)g_p(z, z'; Q) = 0 \quad (4.1)$$

where the appropriate form of $u(z)$ has been used, namely (2.13) with (2.15a). In case of no boundaries the correct solution of the above equation that reduces to the δ -function in the limit of $t \Rightarrow 0$ is obtained as

$$g_p(z, z'; Q) = \frac{e^{-w|z-z'|}}{2w} \quad (4.2)$$

where

$$w^2 = Q^2 + 2\alpha^2 + p. \quad (4.3)$$

As we introduce the boundaries g_p and its first derivative should remain continuous across $z = \pm a$. In the region $|z| > a$ there are no ions and $\alpha = 0$. This condition leads to the following form of the Green ('heat') function

$$g_p(z, z'; Q) = \frac{e^{-w|z-z'|}}{2w} + \frac{\gamma}{w} \left[\frac{\cosh wz \cosh wz'}{(e^{2wa} - \gamma)} + \frac{\sinh wz \sinh wz'}{(e^{2wa} + \gamma)} \right] \quad (4.4)$$

with

$$\gamma = \frac{(Q^2 + 2\alpha^2 + p)^{1/2} - (Q^2 + p)^{1/2}}{(Q^2 + 2\alpha^2 + p)^{1/2} + (Q^2 + p)^{1/2}} = \frac{w - w_0}{w + w_0}. \quad (4.5)$$

The evaluation of Tr is now straightforward and can be cast into a very simple form, namely

$$\operatorname{Tr} G(\mathbf{r}, \mathbf{r}'; t) = \frac{S}{2\pi} \int_0^\infty \mathcal{L}^{-1}[\operatorname{Tr} g_p(z, z'; Q)] Q dQ. \quad (4.6)$$

It is easy to show furthermore that $\operatorname{Tr} g_p$ satisfies the following identity:

$$\operatorname{Tr} g_p(z, z'; Q) = \frac{\partial}{\partial \alpha^2} I(\alpha^2, p) \quad (4.7)$$

with

$$I(\alpha^2, p) = 2a(w - w_0) + \ln(1 - \gamma^2 e^{-4wa}) - \ln(1 - \gamma^2). \quad (4.8)$$

The free energy (3.12) can also be evaluated in closed form in this limiting case yielding

$$F = \frac{kTS}{4\pi} \int_0^\infty Q \, dQ [I(\alpha^2, p=0) - I(\alpha^2=0, p=0)]. \quad (4.9)$$

It is not surprising that this result coincides with the formula derived through the WKB approximation [4, equation (70)] since this approximation is exact in the limit $a \Rightarrow 0$. With substitution $(Qa)^2 = u^2 \sinh^2 t$, where $u = (2\alpha a)^{1/2}$, and a partial integration, the free energy (4.9) can be rewritten in an equivalent form

$$\frac{F}{S} = -\frac{kT2a}{4\pi3} \left(\frac{2\Gamma}{a}\right)^{3/2} + \frac{kTu^2}{4\pi a^2} \int_0^\infty \sinh t \cosh t \, dt [\ln(1 - e^{-4t-4u \cosh t}) - \ln(1 - e^{-4t})]. \quad (4.10)$$

We now have to evaluate the appropriate expansion of the above integral in the limit $u \Rightarrow 0$. As can be demonstrated, the third-order term in u of the second expression in (4.10) exactly cancels the first term; the correct expansion for F therefore starts with a fourth order term in u , the exact form being

$$\frac{F}{S} \approx \frac{kT}{4\pi} \frac{u^4}{a^2} \ln(u) = \frac{kT}{4\pi} \Gamma^2 \ln(4\Gamma a). \quad (4.11)$$

This expression is clearly not analytic in u and that is the reason why the expansion of the same integral quoted in [4, equation (71)] was not derived correctly. Equation (4.11) is the final expression for the first-order (in kT) correction to the mean-field free energy of an inhomogeneous counterion-only system in the limit of small coupling.

5. The limit of large coupling ($\Gamma a \Rightarrow \infty$)

There is a certain essential simplification in this limit that we want to discuss first. A look at the mean-field solution (2.13) shows that in the large-coupling limit the potential in the 'heat' equation (3.8) becomes infinitely large close to the boundaries $z = \pm a$. The region $|z| < a$ becomes therefore basically decoupled from the rest of the volume and the surfaces begin to act like ideally polarisable boundaries that do not allow the penetration of the electric field. This fact greatly simplifies the calculation of the Green function $g(z, z'; Q, t)$ of the 'heat' equation in this limit.

Since in the large-coupling limit different Q -modes within the $|z| < a$ slab and outside of it are decoupled it is very convenient to express the Green function of the 'heat' equation in the form of a functional integral

$$g(z, z'; Q, t) = \int_{z(t)} \exp\left(-\frac{1}{4} \int_0^t \left(\frac{dz}{dt}\right)^2 dt - \int_0^t V(z) dt\right) \mathcal{D}z(t) \quad (5.1)$$

where $\mathcal{D}z(t) = \lim_{n \Rightarrow \infty} dz(t_1) dz(t_2) \dots dz(t_N)$ and

$$V(z) = Q^2 + u^2(z). \quad (5.2)$$

The propagator (5.1) represents diffusion in an external field or a quantum mechanical particle in an external potential moving in imaginary time. With a change of variable

$z \Rightarrow 2z - a$ the functional integral (5.1) can be transformed into the propagator of the Pöschl-Teller potential solved analytically by Inomata and Kayed [9]. Using their general result for the propagator of a one-dimensional quantum mechanical particle, in an external potential of the form

$$V(z) = 2V_0\lambda(\lambda - 1)\sin^{-2} 2z$$

derived on the basis of a special coordinate and 'time' transformation in the functional integral (5.1), we can obtain the following form of the 'heat' function (5.1):

$$g(z, z'; Q, t) = e^{-Q^2 t} 2a(\cos \alpha z \cos \alpha z')^{1/2} \sum_{N=0}^{\infty} \Delta_N(z, z') e^{-\alpha^2(N+2)^2 t} \quad (5.3)$$

where

$$\Delta_N(z, z') = (N+2) \frac{(N+3)!}{N!} P_{N+3/2}^{-3/2}(\sin \alpha z) P_{N+3/2}^{-3/2}(\sin \alpha z')$$

with $P_i^k(x)$ being the associated Legendre functions. We can now insert this expression into (3.9) to obtain the free energy. Before doing that we make use of the orthogonality properties of the associated Legendre functions, remaining with

$$\text{Tr } G(\mathbf{r}, \mathbf{r}'; t) = \frac{S}{2\pi} \int_0^\infty \text{Tr } g(z, z'; Q, t) Q \, dQ = \frac{S}{4\pi} \frac{1}{t} \sum_{N=0}^{\infty} e^{-\alpha^2(N+2)^2 t}. \quad (5.4)$$

$\zeta_A(s)$, equation (3.5), can now be evaluated straightforwardly. First of all we use the integral representation of the Riemann zeta function $\zeta(s)$

$$\int_0^\infty t^{s-1} \sum_{n=1}^{\infty} e^{-n^2 t} \, dt = \zeta(2s) \Gamma(s).$$

Next we reduce (5.4) to a form that will allow the application of the above Riemann integral, which amounts to a displacement of the origin of the N summation. Now the use of the Riemann integral allows us to write

$$\zeta_A(s) = \frac{S}{4\pi} \frac{\Gamma(s-1)}{\Gamma(s)(\alpha^2)^{s-1}} [\zeta(2(s-1)) - 1]. \quad (5.5)$$

Therefore

$$\zeta'_A(s=0) = \frac{S}{4\pi} [(\alpha^2 \ln(\alpha/\Gamma))^2 - \alpha^2(\zeta(-2) - 1) - 2\alpha^2 \zeta'(-2)].$$

Invoking again (3.9) and the basic properties of the Riemann zeta function [10] we can obtain for the free energy in the limit of large coupling the following expression:

$$\frac{F}{S} = -\frac{kT}{2} \frac{d\zeta_A(s=0)}{ds} = \frac{kT}{4\pi} \left[\alpha^2 \ln(\alpha/\Gamma) - \frac{\alpha^2}{2} - \frac{\zeta(3)}{4(2a)^2} \right]. \quad (5.6)$$

In the last term of the above equation we can clearly recognise the zero-order term of the van der Waals interaction between two ideally polarisable surfaces at separation $2a$ [1]. This is not surprising since we noted that in the large-coupling limit the surfaces

ideally screen the spatial regions $|z| > a$ from electric fields. The other terms are due to the fluctuations of the local electrostatic potential around its mean-field value.

6. Discussion

In this work we have improved the standard Poisson-Boltzmann result for the interaction of two electrified surfaces immersed in a counterion-only Coulomb fluid by going one order beyond the mean-field result. Our approach was based on a functional integral representation of the grand canonical partition function that allows the application of standard field-theoretic approaches. The limiting cases of small and large couplings have allowed a derivation of simple analytic results.

The same problem has recently been treated by Attard *et al* with standard statistical mechanical methods. Their result (equation (3.14) of [11]) in the large-coupling limit is similar to our (5.6) except for a spurious factor of $\pi/4$. This difference is, however, not trivial. This can be most easily seen by inspecting (4.8), which is valid in the opposite limit but nevertheless proves our point. We showed [4] that the first term corresponds to a generalisation of the bulk (Debye-Hückel free energy in the case of uni-univalent electrolyte) free energy, the third one to a generalisation of the surface (Onsager-Samaras free energy in the case of uni-univalent electrolyte with image interactions) free energy and the second one is nothing but the log of the secular determinant. Of these three terms the result of [11] contains only the second one; the dependence of pure bulk and pure surface modes on intersurface separation was therefore ignored. The situation is somewhat similar to the case of van der Waals interactions in media with a spatially dispersive dielectric function [12]. There too the bulk modes depend on the intersurface separation and their contribution should be included into the interaction free energy. However, in the asymptotic regime ($a \Rightarrow \infty$) the first and the third terms of (4.8) become unimportant, and the result derived by Attard *et al* should be asymptotically correct. This clearly is the case (see (5.6) in the strict limit $a \Rightarrow \infty$).

Finally let us just quote the total interaction free energies that we derived in the saddle-point approximation. In the small-coupling limit the sum of (2.6) and (4.11) gives

$$\frac{F}{S}(\Gamma a \Rightarrow 0) \approx -4kT \frac{\Gamma}{L_B} \left(1 - \frac{L_B \Gamma}{16\pi} \right) \ln(\Gamma a).$$

This form of the free energy could be interpreted in the sense that the value of the surface charge density is renormalised due to the fluctuations in the local electrostatic fields as the two surfaces come close together. In the opposite limit the sum of the mean-field and the fluctuation contribution gives to the lowest order

$$\frac{F}{S}(\Gamma a \Rightarrow \infty) \approx kT \left[\frac{\pi^2}{aL_B} - \frac{1}{4\pi} \left(\frac{\pi}{2a} \right)^2 \ln(\Gamma a) \right].$$

This limiting form suggests the interpretation that the effective intersurface separation is renormalised due to the action of the fluctuations.

We can end our contribution on an optimistic note by hoping that the field-theoretic approach to the interaction of electrified surfaces in Coulombic fluids opens new possibilities for the more powerful methods, already amply used in solid state physics, to be applied to this type of problem.

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